

Juxtaposition of Spin Freezing and Long Range Order in a Series of Geometrically Frustrated Antiferromagnetic Gadolinium Garnets

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Specific heat measurements in zero field are presented on a homologous series of geometrically frustrated, antiferromagnetic, Heisenberg garnet systems. Measurements of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, grown with isotopically pure Gd, agree well with previous results on samples with naturally abundant Gd, showing no ordering features. In contrast, samples of $\text{Gd}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ are found to exhibit clear ordering transitions at 243 mK and 175 mK respectively. The effects of low level disorder are studied through dilution of Gd^{3+} with non-magnetic Y^{3+} in $\text{Gd}_3\text{Te}_2\text{Li}_3\text{O}_{12}$. We discuss possible explanations for such diverse behavior in very similar systems.

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Magnetic systems of spins residing on the sites of a lattice of corner-sharing simplexes, such as triangles or tetrahedra, coupled via a nearest-neighbor (n.n.) antiferromagnetic Heisenberg exchange Hamiltonian, \mathcal{H}_0 , are highly frustrated. The spins are unable to minimize their energy pair by pair and, at the classical level, such a model results in a sort of “spin liquid” state without long range order (LRO) and with zero net magnetic moment, \mathbf{M}_s , on each simplex [1]. Perturbations to \mathcal{H}_0 , \mathcal{H}' , such as exchange beyond n.n. and dipolar interactions, perhaps assisted by thermal and/or quantum fluctuations, are expected to lift the classical ground state degeneracy and drive the system into a state of LRO. However, the ground state remains extremely fragile against quenched disorder and as a result, rather than developing LRO, the combination of high frustration and weak random disorder can in principle [2, 3] and in practice, for example in the pyrochlore $\text{Y}_2\text{Mo}_2\text{O}_7$ (YMO) [4, 5], cause a system to exhibit a spin glass transition. One might quickly conclude that the glassy physics of the highly frustrated magnet (HFM) $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG), a hyperkagomé network of corner-sharing triangles, is the result of a similar situation. However, the glassy behavior of YMO seems largely conventional [4] whereas GGG is known to display highly exotic properties that incorporate unconventional spin glass behavior [6] coexisting with extended short range order [7] and low temperature spin fluctuations [8].

Thus one is led to consider the much more exciting possibility that the presence of several interaction terms of different spatial range and anisotropic nature that make up \mathcal{H}_0 and \mathcal{H}' may, through their competition, lead to a complex energy landscape causing glassy behavior that is not induced by quenched randomness [9]. Such a phe-

nomenon parallels a theoretical description of *structural* glasses that builds on the notion of locally preferred structure in a liquid that is frustrated at large length scale due to its inability to suitably fill space, hence inhibiting the formation of a crystalline state and leading to a glass transition [10]. Could a HFM system, with its locally satisfied $\mathbf{M}_s = 0$ simplexes, display a disorder-free freezing akin to the glass transition when subject to the competition of the terms that constitute \mathcal{H}' ? This may be well realized in a system like GGG where the dominant local Heisenberg exchange is in competition with the also important long range dipolar interaction [11, 12].

The amount of disorder in GGG is low, consisting of up to a possible 1-2% off-stoichiometry of Gd^{3+} magnetic ions on otherwise non-magnetic Ga^{3+} sites, inherent in crystal growth [13]. There has so far been no theoretical explanation for the glassiness seen in GGG, thus it is crucial to ascertain whether the behavior in GGG is an intrinsic property of Gd^{3+} ions on the garnet lattice arising from competing antiferromagnetic short range exchange and long range dipolar interactions or whether a generic 1-2% random disorder is responsible for the glass transition. In this Letter, we investigate this question using specific heat measurements to study a homologous series of three Gd garnet materials: the aforementioned GGG as well as $\text{Gd}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ (GTLG) and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ (GAG). Additionally, we have tested the effects of random chemical substitution of non-magnetic Y^{3+} for Gd^{3+} in GTLG to investigate in a controlled manner a level of disorder comparable to or higher than that of GGG. Our results show that spin glass behavior resulting from a generic sensitivity to disorder is too simple a picture for this particular series of materials.

We have measured a single crystal of GGG, made from

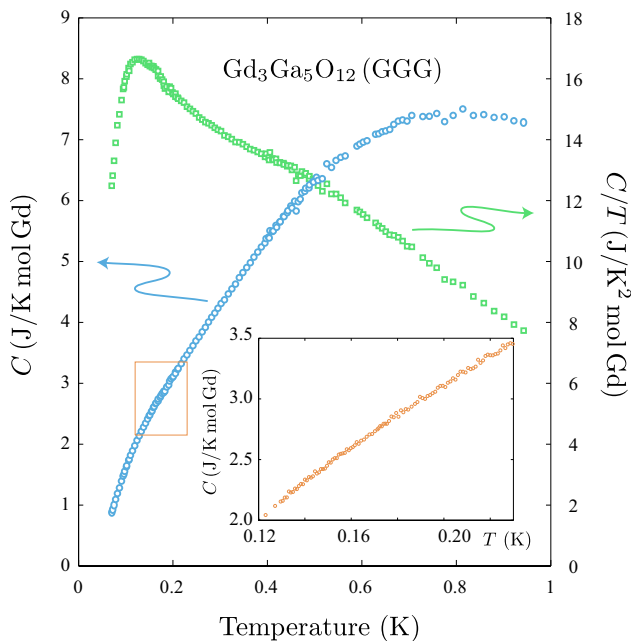


FIG. 1: (color online) Specific heat (C) and C/T of isotopically pure GGG measured with coarse temperature resolution. Results match well with previous work [6]. The temperature region marked with a red box has been remeasured with a high temperature resolution shown in the inset and again does not find evidence of an ordering transition.

isotopically pure ^{160}Gd , grown from the same powder used for neutron scattering measurements [7, 14]. Preparation of this sample has been described in Ref. [15]. The samples of GTLG and GAG were polycrystalline samples made from naturally abundant Gd. GTLG samples were made by solid-state reaction in air of Te and Gd (Y) oxides and Li carbonate, pressed into pellets, at 850 C for 10 hours, then regrinding and firing a second time. The polycrystalline sample of GAG was made using the sol-gel method [16]. It was heated to 1350 C for one hour, then removed from the furnace and rapidly quenched to room temperature, to minimize the formation of perovskite-phase GdAlO_3 [17]. Powder x-ray diffraction spectra in both cases could be indexed to space group $\text{Ia}\bar{3}\text{d}$. No impurity peaks were visible at the 1% level in GTLG; in GAG, there were two impurity peaks attributed to GdAlO_3 , at the 3% level.

Specific heat, C , measurements were performed at dilution refrigerator temperatures, using the quasi-adiabatic method as in Refs. [18, 19], with thermometer and heater fixed directly to the samples. 6 μm diameter, ~ 1 cm long superconducting leads were used to provide excellent thermal isolation. A long time constant of relaxation ($\tau > 1$ hour) ensured that internal temperature gradients due to poor thermal conductivity (of particular concern in the powder samples) were not a significant source of systematic error.

An initial measurement of C of GGG was made over a large temperature range (from 80 mK to 930 mK) using temperature steps of roughly 5 mK below 200 mK and temperature steps of 10 mK above 200 mK. Results of our specific heat measurements on GGG, shown in Fig. 1, agree remarkably well with the previous specific heat measurement (on a single crystal containing naturally abundant Gd) of Schiffer *et al.* [6]. We find a broad feature with a maximum at around 800 mK. This feature seems to drop out at lower temperature roughly as $T^{0.8}$ until around 125 mK, at which point there is a maximum in C/T and $C(T)$ becomes steeper. The specific heat measurement of Dunsiger *et al.* on a naturally abundant Gd, powder sample is very similar, though the peak in C/T is found to be more pronounced [8]. This result suggests that the isotopically pure sample measured here exhibits the same physics as do naturally abundant Gd containing samples and reconfirms the absence of a sharp ordering feature in C that would indicate a transition to LRO.

Other experiments by Schiffer *et al.* on GGG have suggested the material to be a spin glass, albeit a somewhat unconventional one [6]. The spin glass interpretation is largely based on glassy relaxation in the ac susceptibility and a sharp peak in the nonlinear susceptibility (χ^3) at around 180 mK [6]. However, there is also a broader peak in χ^3 at 450 mK and there is no corresponding maximum in the specific heat (as seen in Fig. 1) but just a maximum in C/T at around 120 mK.

There is also a collection of experiments that provide evidence *against* a spin glass transition. μSR and Mössbauer experiments, for example, show significant persistent spin dynamics (PSDs) down to temperatures as low as 25 mK [8, 20, 21]. Most curiously, neutron scattering experiments on GGG, possible only with samples made from isotopically pure ^{160}Gd that does not absorb neutrons, have shown sharp diffraction peaks developing below 140 mK [7, 14]. Though these peaks are not sharp enough to imply true long range order (LRO), they suggest magnetic ordering with a correlation length of at least 100 Å. This has been suggested to be a type of mixed spin liquid/solid state [7]. Bulk dynamical measurements have also been interpreted as a signature of an ordering transition [22]. Recent inelastic neutron scattering measurements have revealed three gapped dispersionless excitations are found, two of which can be attributed to dimerized antiferromagnetic order [23].

In a theoretical study [11, 12], aiming to relate the sharp features in the GGG neutron scattering pattern [7] with a long-range ordered state, the spin-spin correlations were treated using mean-field theory and using an Ewald summation method to handle the important dipolar interactions. Tuning the second (J_2) and third (J_3) n.n. couplings and simulating the powder neutron diffraction signal, Ref. [11] was able to find excellent agreement with experiment, thereby determining optimal

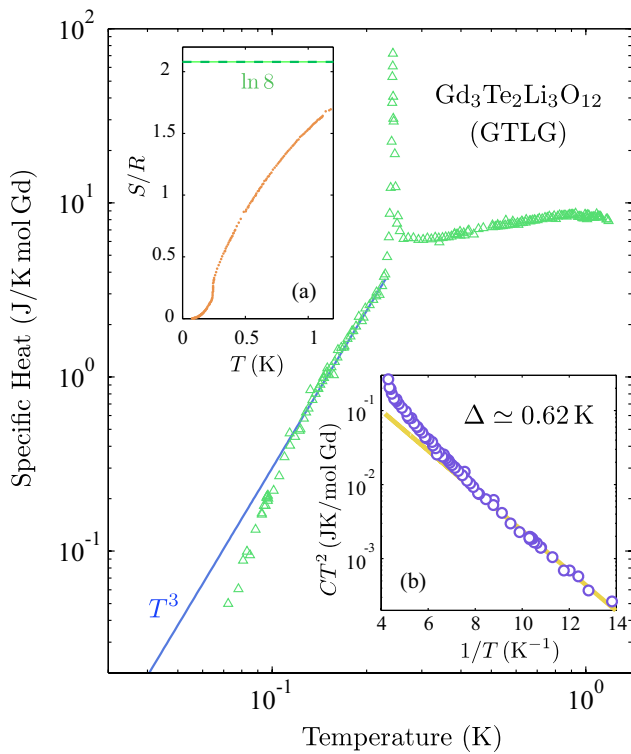


FIG. 2: (color online) Specific heat of GTLG showing a sharp first-order phase transition. The specific heat drops out quicker than T^3 below T_c . Inset (a) shows the entropy as a function of T compared with the total $R \ln 8$ entropy in the system. Inset (b) shows CT^2 as a function of T^{-1} and a linear fit suggestive of spin waves with a gap of $\Delta = 0.62$ K.

interaction strengths. Most interestingly, it was found that the system exhibits a quasi-degeneracy critical (soft) modes, suggesting that this enhances fluctuations and makes it very sensitive to small amounts of disorder [12].

This apparent development of rather long range order [7] and its seeming consistency with theory [11, 12] makes the lack of an ordering transition in specific heat measurements very paradoxical indeed. In order to address this problem, we have performed an additional measurement using a much higher temperature resolution of 1 mK over the temperature range 130 mK to 230 mK to search for small or narrow features near where the neutron scattering peaks were discovered that might have been previously missed. This choice of resolution is based on scaling results of well characterized antiferromagnets to a transition temperature of 140 mK, suggesting one might expect a peak in C with a width of only several mK. However, the high-resolution scan of C , shown in the inset of Fig. 1, also does not reveal any anomalies that might be interpreted as an ordering transition.

In stark contrast, GTLG displays a sharp transition at 243 mK as shown in Fig. 2. This is close to the temperature (~ 250 mK) where a feature was previously observed

in the magnetic susceptibility of GTLG [24]. The transition is clearly first-order, exhibiting a much sharper peak in C than could be expected for a continuous phase transition. With a Curie-Weiss temperature $\theta_{CW} \simeq -2.7$ in GTLG [24], this ordering temperature gives a frustration index $f = \theta_{CW}/T_C = 11$. Below the transition, C drops out faster than T^3 suggesting that it is exponential and that there are gapped spin wave excitations, as would be expected from LRO with a strong dipolar interaction [19, 25]. Gapped spin waves should result in a low temperature behavior $C \propto T^{-2}e^{-\Delta/T}$, thus we plot CT^2 vs. $1/T$ in inset (b) of Fig. 2. The resulting linear fit gives $\Delta \simeq 0.62$ K. Above the transition, there is a broad feature centered around roughly 1.0 K, similar to the broad feature in GGG centered at ~ 0.8 K (see Fig. 1) and is likely a signature of the development of short range correlations. Obtaining the entropy (S) from a numerical integral of C/T shows that only about 14% of the total $R \ln 8$ entropy in the system is accounted for by the transition, as shown in inset (a) of Fig. 2.

The third material studied here, GAG, may represent a point in between GGG and GTLG with a smaller and broader transition at a lower temperature of 175 mK (shown in Fig. 3). With $\theta_{CW} \simeq -3.0$ K [26], it is more antiferromagnetic than the other two garnets, but seemingly more frustrated than GTLG, with a frustration index $f = 17$. Otherwise, it shows similar features to GTLG, with a broad maximum centered around 1 K and a steeply dropping specific heat at lower temperatures. As in GTLG, the transition in GAG accounts for only a small percentage of the total $R \ln 8$ entropy in the system. The smaller and broader transition may be the result of the small level of GdAlO_3 impurities.

It seems likely that GTLG does not have the same off-stoichiometry that is found in GGG, making it a “cleaner sample”; Gd^{3+} ions are unlikely to take the place of Li^+ or Te^{6+} ions as easily as Ga^{3+} ions. Thus, we have added a low level of disorder to GTLG through dilution of Gd^{3+} ions with non-magnetic Y^{3+} ions. This “dirty” GTLG sample shows a significantly broadened peak but *no* significant change in the peak temperature, as shown in Fig. 3. At temperatures well below and well above the transition, C of the pure and diluted samples match, and the transition accounts for the same amount of entropy in both systems, suggesting that the ground state ordering is not appreciably altered by the 2% impurity.

In conclusion, despite their similar models, we find GTLG and GAG to in fact behave entirely differently from GGG. The only commonality in all three systems is the broad feature signaling short range correlations at around 0.8 K in GGG and 1.0 K in GAG and GTLG. The lower temperature of the broad feature in GGG is consistent with its smaller nearest neighbor exchange interaction $J_1 = 0.107$ K [11, 27] as compared to $J_1 = 0.126$ K for GTLG [24] and $J_1 = 0.142$ K for GAG [26].

The sharp features observed in GTLG and GAG are

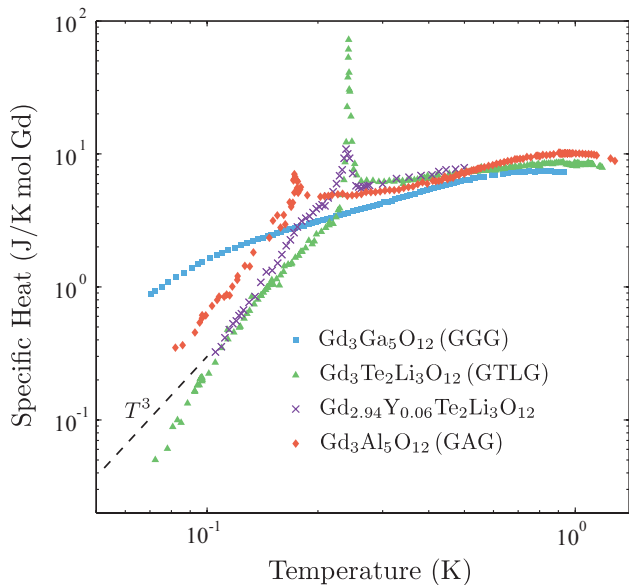


FIG. 3: (color online) Comparison of the specific heat of GGG (blue squares), GTLG (green triangles), GAG (red diamonds) and a sample of 2% diluted GTLG (violet x's).

in all likelihood signatures of transitions to long range order. In fact the majority of insulating rare-earth garnets studied [28–30] exhibit transitions to a magnetically ordered state [31]. An exponential drop in the specific heat below the transitions, indicative of gapped spin-wave excitations, also provides strong evidence of LRO. Such behavior is reminiscent of the Gd pyrochlore material $\text{Gd}_2\text{Sn}_2\text{O}_7$ which also shows a sharp first-order phase transition to a ground state exhibiting static magnetic order and well-defined excitations as seen by neutron scattering [32] and specific heat experiments [19].

The materials GTLG and GAG clearly do not share the same glassy physics as GGG since spin glasses are universally found to *not* exhibit a sharp peak in C [33]. These results prove that the glassy physics of GGG is not a ubiquitous property of Gd garnets and we are therefore left with two possible conclusions. First, a very precise tuning of the parameters of the Hamiltonian may be required in order to produce the necessary competition between local and long range interactions to give rise to a magnetic analog of the glass transition, even without quenched disorder. GTLG and GAG may be outside this narrow “window” of required parameter space. However, in many glass forming liquids (see for example [34]) it is found that tuning interaction strengths, for instance by altering the substituents of molecules, without changing the overall symmetry of those molecules, does not tend to preclude the glass transition.

A plausible alternative is that it is indeed a sensitivity of the system to small levels of disorder that results in a spin glass transition in GGG. Since the ordered ground

states of GTLG and GAG appear to be robust against levels of random dilution at least as high as those in GGG, it seems that the *type* of disorder may be the crucial ingredient in the exotic behavior of GGG. In other words, the random excess of Gd on Ga sites, found in GGG, may be a much more powerful way to introduce random frustration and trigger a spin glass transition than simple dilution of the magnetic moments. This work shows that the response of a HFM to random disorder can be highly nontrivial, and a function of the nature of that disorder in concurrence with the nature of the interactions present.

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